

Nano-structured lithium-tin plane fabrication for laser produced plasma and extreme ultraviolet generation

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Abstract

This paper deals with a lithium/tin combined target to increase the conversion efficiency of extreme ultraviolet (EUV) of 13.5 nm emission from laser-produced plasma. The bilayer target of glass/lithium (20 nm)/tin (50 nm) exhibits a sharp and strong emission in comparison with a Sn bulk target. The reverse coating of glass/tin/lithium was unstable and EUV could not be observed. By using nano-porous SnO₂ and an electrochemical deposition of lithium, nano-structured lithium/tin composite was prepared, and was stable without deliquescence of lithium.

Keywords: EUV; lithium; low density

1. INTRODUCTION

Extreme Ultraviolet (EUV) Lithography has been identified as one of the key technologies for advancement of the integrated circuit manufacturing industry along the technical path based on the international technological roadmap for semiconductors (ITRS) (Bakshi *et al.*, 2006). According to ITRS, EUV is the first candidate for the half pitch size of 32 and 22 nm. The light source of 13.5 nm is one of the critical issues for the practical EUV lithography. Laser produced plasmas give EUV generation, owing to the heating of target by a laser pulse (Sizyuk *et al.*, 2007; Orlov *et al.*, 2007; Kolacek *et al.*, 2008; Nagai, 2008). In Japan, a leading project for development of the EUV light source for advanced lithography technology by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) with relevance to the EUV lithography system development association (EUVA) under auspices of the Ministry of Economy, Trade and Industry (METI) was to accelerate the development of a EUV lithography system. Our institute (ILE, Osaka University) has started intensive research on the laser-produced plasma (LPP) source. In LPP, the target material is heated by a laser pulse to generate high-temperature plasma. Xenon, tin, and lithium have been target materials of choice for EUV sources. The project

found the highest conversion efficiency (CE) from laser light to EUV using a tin target (Shimada *et al.*, 2005).

$$CE = \int_0^{2\pi} \int_0^{\pi/2} E_{EUV}(\theta) d\theta d\Omega, \quad (1)$$

where $E_{EUV}(\theta)$ means the ratio of EUV 2%-energy per steradian in band at 13.5 nm monitored at an angle of θ to the irradiated laser energy. To control plasma density, low density and porous materials are often used as laser targets. Figure 1 shows the highest CE is given for the density of tin plasma to be $10^{18} - 10^{19}$ ions/cm³, with electron temperature of ~ 40 eV as shown in Figure 2 (Nishihara *et al.*, 2006, 2007). Such plasma can be produced from low-density materials efficiently.

Low-density materials are widely used as laser targets in relevant to shock, laser plasma interaction, and laser fusion experiments (Nagai *et al.*, 2004a, 2005; Khalenkov *et al.*, 2006; Xu *et al.*, 2006; Batani *et al.*, 2007; Bagchi *et al.*, 2008; Yang *et al.*, 2008). Actually, low-density effects were found as monochromatic EUV emission, using porous and nano-structured SnO₂ (Nagai *et al.*, 2004b; Tao *et al.*, 2004; Okuno *et al.*, 2006; Pan *et al.*, 2006), flying particles (Uchida *et al.*, 2005; Aota *et al.*, 2005), tin dispersed plastics (Harilal *et al.*, 2006; Hayden *et al.*, 2006), and tin dispersed droplet (Higashiguchi *et al.*, 2007). The corresponding target fabrication methods have been investigated (Hund *et al.*, 2006; Gu *et al.*, 2006; Nagai *et al.*, 2006a; Yasuda *et al.*,

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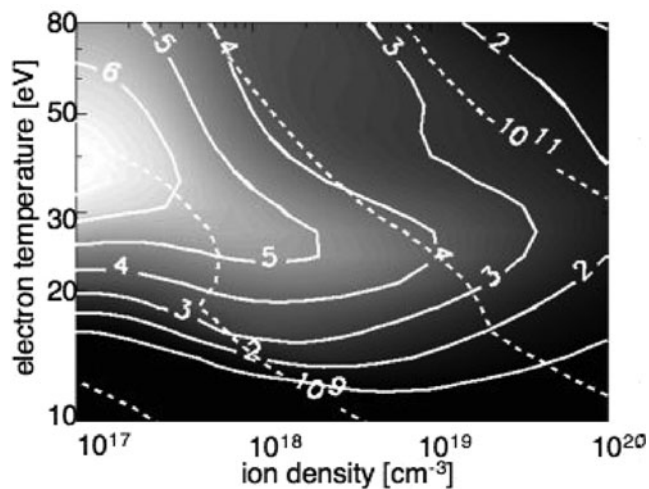


Fig. 1. Dependence of conversion efficiency (white line Contours of the CE obtained from the power balance model in the plane of ion density (n_i) and electron temperature (T_e) with pulse duration of 5 ns and laser wavelength of 1.064 μm . Dashed lines: %) in required laser intensity (dotted lines: W/cm^2). Reprinted with permission from K. Nishihara *et al.*, Annual Progress Report 2006 of Institute of Laser Engineering, Osaka University, pp. 9, (2007). Copyright © K. Nishihara.

2006, 2007). Recently, nano- and micro-structure effects were found in laser produced EUV applications (Nagai *et al.*, 2006b).

On the other hand, lithium LPP has a simple line emission and an intense line within 2% bandwidth around 13.5 nm that is based on the $1s-2p$ Lyman α transition in excited Li^{2+} ions where the electron temperature is 15–18 eV. The ionization energy of the lithium ion is much smaller than that of xenon and tin. This means that the absorption energy is much less wasted in the lithium LPP compared to Xe and Sn LPP. To increase the lower CE of Li LPP, a forced recombination method is invented (Nagano *et al.*, 2007) where Li^{3+} ions were cooled by low temperature electrons from

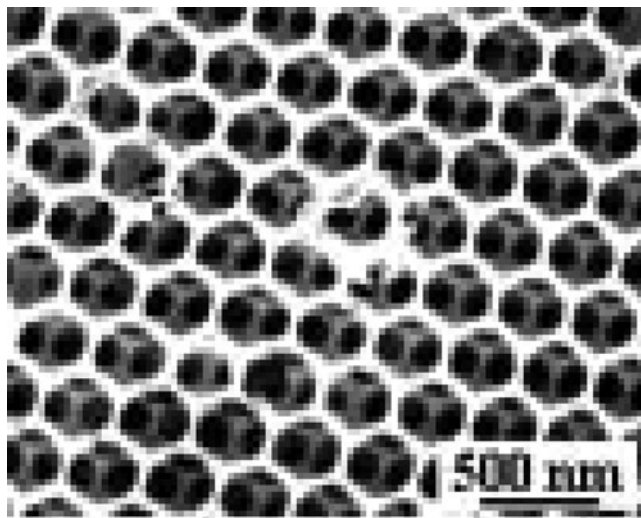


Fig. 2. SEM image of a porous SnO_2 prepared from nanoparticles template.

a tamper and converted to excited Li^+ . In view of the CE depending on different LPP temperatures for Sn and Li, a combination of Sn and Li might serve as an efficient target, i.e., Sn should be heated by laser and Li is heated by the remnant thermal energy of Sn ions. Here we introduce the combined targets of Sn and Li and a fabrication.

2. EXPERIMENT SECTION

2.1. Materials

Lithium/tin bilayer was prepared by thermal vapor deposition on a glass plate. Nano-structured lithium/tin composite was prepared as follows. The first porous tin oxide was prepared on platinum coated glass plate by polystyrene nanoparticles template and sol-gel method using liquid tin(IV)chloride (Nagai *et al.*, 2004b, Gu *et al.*, 2005). The porous SnO_2 mandrel had a ~ 300 nm pore size, which was almost the same as the particle size of mandrel polystyrene nano-particles. The average density of the nanoporous SnO_2 was $1.5 \text{ g}/\text{cm}^3$, which was 23% of the density of SnO_2 bulk. The density ratio corresponds well to the rest of the highest packing density (76%) of nanoparticles. The relative tin content was estimated to be $\sim 17\%$, respectively, per bulk tin (β phase) content. The typical thickness of the porous SnO_2 was 100 μm . The second, the porous SnO_2 was soaked in electrolyte consisting of LiClO_4 propionic carbonate solution. The applied potential was -3.0 V versus the reference electrode of lithium metal.

2.2. Measurements

Electrochemical plating was done using potentiostat HABF 501 (Hokuto Denko). The scanning electron microscopy (SEM) image was taken by JSM 7400 FS (JEOL). EUV plasma generation was carried out using an Nd:YAG laser whose pulse width was 10 ns. The focal spot diameter was fixed at 500 μm . The laser pulse energy was $6 \times 10^{10} \text{ W}/\text{cm}^2$. The incident angle of the laser beam was normal to the target front face. A target sample area was kept at $\sim 4 \text{ mm}^2$. A grazing incident spectrometer (GIS), including a varied-line-space concave grating of 1200 line/mm grooves, was used to observe EUV emission spectra in the range of 6–20 nm. The output spectrum was recorded with a back-illuminated CCD camera and the spectral resolution was 0.06 nm at 13.5 nm.

3. RESULT AND DISCUSSION

3.1. EUV Emission From Lithium/Tin Bilayer

Figure 3 shows the emission spectra for bulk tin (a) and lithium/tin bilayer (b). The intensities were normalized by the incident laser power. An emission is seen around 13.5 nm, which is close to the previously reported wavelength, and is characteristic of the radiations from Sn^{6+} to

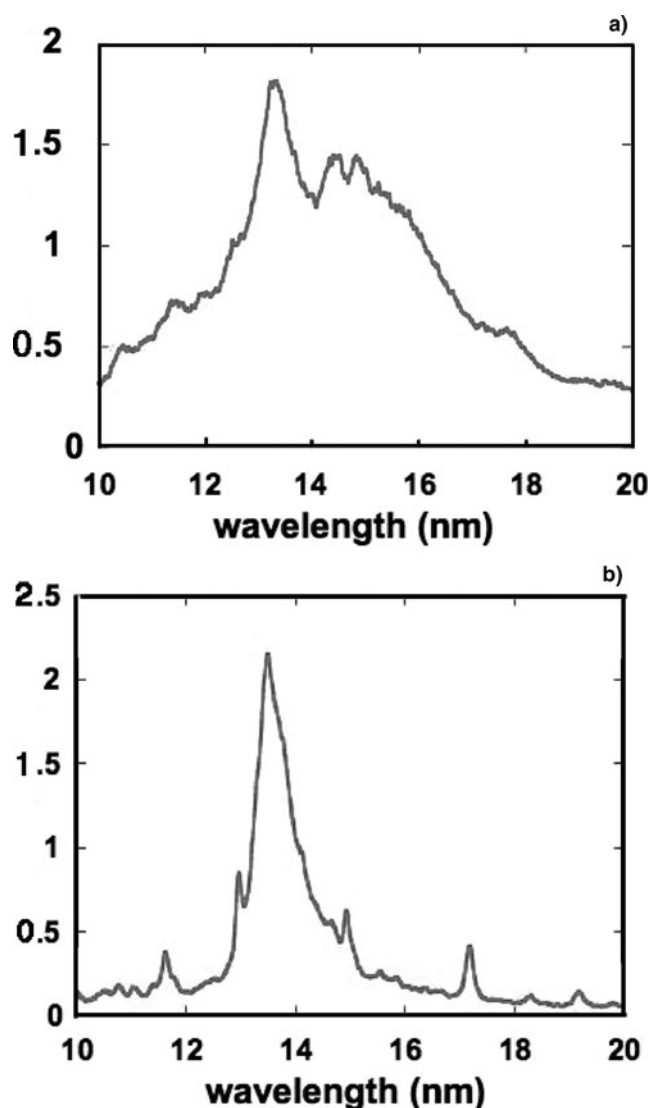


Fig. 3. EUV emission spectra from bulk tin (a) and lithium/tin (20 nm/50 nm) bilayer targets measured by a grazing incident spectrometer.

Sn^{13+} . The dip of emission at 13.5 nm has been characterized as a strong re-absorption by corona plasma (so-called opacity effect) (Fujioka *et al.*, 2005a). According to these studies, the opacity, as well as emissivity, of laser-produced Sn plasma is quite high for 13.5 nm light. In optically thick Sn plasma, a portion of the incident laser energy used for heating a deep region of plasma is not efficiently converted into the output EUV energy. Therefore, optically thinner plasma emits 13.5 nm light more efficiently; otherwise the intensity of 13.5 nm light is limited by the black-body intensity depending only on electron temperature at the plasma surface. There are several known ways to control the optical thickness of plasmas. One is the use of low density target. In the cases of 10 ns pulse, the highest CE of 2.2% was obtained at the optimum intensity of $5 \times 10^{10} \text{ W/cm}^2$ for the 0.5 g/cm^3 low-density SnO_2 targets (Nagai *et al.*, 2006b; Okuno

et al., 2006). The peak CE for the low-density SnO_2 targets was 1.7 times higher than that for the solid-density Sn targets. In the study of the dynamics of plasma expansion (Okuno *et al.*, 2006), with changing initial target densities, the distance between the EUV emission-dominant region and the plasma surface becomes shorter for lower density targets. It was explained that the shortening results in the efficient EUV emission, because less 13.5 nm light emitted from the emission-dominant region is absorbed in the preceding plasmas before the light reaches the plasma surface. Furthermore, the plasma surface may maintain a relatively higher temperature due to less multidimensional expansion of the plasmas in the case of lower initial density targets.

On the other hand, the present lithium/tin bilayer showed sharp emission at 13.5 nm without dip. Furthermore, the tail of the emission peak is small in comparison to bulk tin. These results imply that a suppression of the re-absorption happened. But, according to the target structure, the re-absorption effect cannot be prevented because the tin layer is coated on the outer layer for the laser incident. To explain the strong emission peak, the contribution of radiation from lithium plasma is necessary. Because the lithium was the backside of the laser incident, the heating can be from the hot tin plasma to the cold substrate of lithium layer. If it is correct, the strong emission is after the re-absorption through hot tin plasma. This result implies much higher CE from the reverse coating of tin/lithium bilayer on a glass substrate. Unfortunately, we have not obtained EUV emission from the opposite bilayer, probably due to the very easy oxidation of metal lithium and deliquescence of lithium hydroxide.

3.2. Nano-Structured Lithium/Tin Composite Fabrication using Electrochemical Plating

In the previous studies, dilute tin in carbon-based plastics also exhibit narrow emission at 13.5 nm with higher CE (Harilal *et al.*, 2006; Hayden *et al.*, 2006), which is similar to low-density tin targets (Nagai *et al.*, 2004b, 2006b; Tao *et al.*, 2004; Okuno *et al.*, 2006; Pan *et al.*, 2006). These phenomena without dip of emission at 13.5 nm have been explained the suppression of re-absorption by a corona plasma as described before. Furthermore, these results of the small difference for the presence of plastics imply that low Z impurity does not affect CE for the tin target, while such carbon gives debris (Fujioka *et al.*, 2005b), which is deposited on the EUV collection mirror. In comparison with carbon debris, lithium is easily removed from the mirror by heating in excess of the boiling point, and has a merit of high emissivity of 13.5 nm in comparison with carbon.

Figure 4 shows the SEM image of the nano-structured lithium/tin composite prepared by an electrochemical method. The backbone of the honeycomb is tin reduced from tin oxide, while the remainder is lithium filled by electrochemical reduction of Li^+ . With a 20 min application of

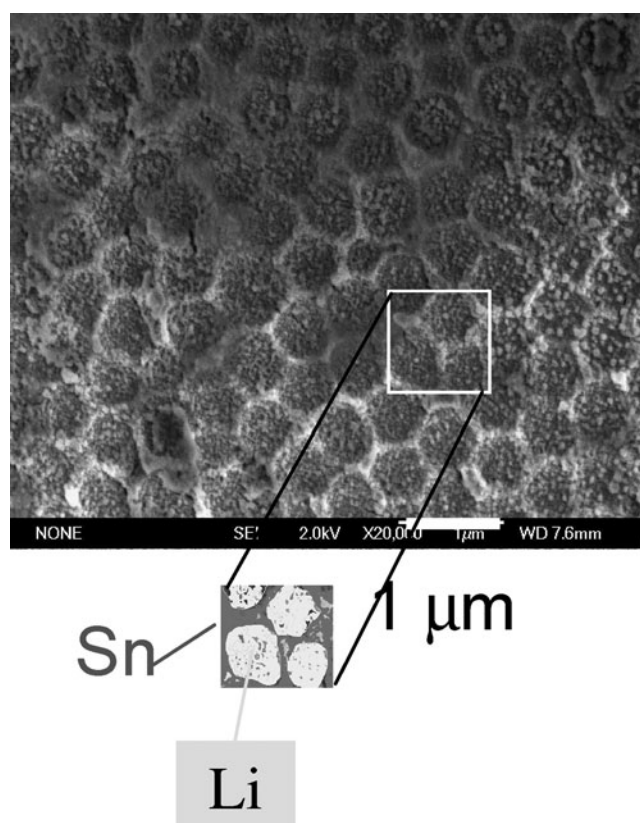


Fig. 4. The SEM image of nano-structured lithium/tin composite prepared from porous SnO₂ as shown in Figure 2.

the potential, a 100 μm thickness was completely filled by lithium. In the case of the present nano-structured composite, and deliquescence of lithium was not observed as seen in the SEM image, implying the stabilization of lithium in the nano-structured pore of Sn network.

4. CONCLUSION

We have proposed a lithium/tin combined target to increase the conversion efficiency of EUV emission from laser-produced plasma. The bilayer target of glass/lithium/tin exhibited sharp and strong emission in comparison with Sn bulk target. The opposite coating of glass/tin/lithium was unstable and EUV could not be observed. By using nanoporous SnO₂ and an electrochemical method, nano-structured lithium/tin composite was prepared, and was stable without deliquescence of lithium.

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REFERENCES

- AOTA, T. & TOMIE, T. (2005). Ultimate efficiency of extreme ultraviolet radiation from a laser-produced plasma. *Phys. Rev. Lett.* **94**, 015004.
- BAGCHI, S., PREM KIRAN, P., BHUYAN, M.K., BOSE, S., AYYUB, P., KRISHNAMURTHY, M. & RAVINDRA KUMAR, G. (2008). Hotter electrons and ions from nano-structured surfaces. *Laser Part. Beams* **26**, 259–264.
- BAKSHI, V. (2006). *EUV Sources for Lithography*. Bellingham: SPIE Press.
- BATANI, D., DEZULIAN, R., REDAELLI, R., BENOCCHI, R., STABILE, H., CANOVA, F., DESAI, Y., LUCCHINI, G., KROUSKY, E., MASEK, K., PFEIFER, M., SKALA, Y., DUDZAK, R., RUS, B., ULLSCHMIED, J., MALKA, V., FAURE, J., KOENIG, M., LIMPOUCH, J., NAZAROV, W., PEPLER, D., NAGAI, K., NORIMATSU, T. & NISHIMURA, H. (2007). Recent experiments on the hydrodynamics of laser-produced plasmas conducted at the PALS laboratory. *Laser Part. Beams* **25**, pp. 127–141.
- FUJIOKA, S., NISHIMURA, H., NISHIHARA, K., MURAKAMI, M., KANG, Y.-G., GU, Q., NAGAI, K., NORIMATSU, T., MIYANAGA, N., IZAWA, Y., MIMA, K., SHIMADA, Y., SUNAHARA, A. & FURUKAWA, H. (2005b). Properties of ion debris emitted from laser-produced mass-limited tin plasmas for extreme ultraviolet source applications. *Appl. Phys. Lett.* **87**, 241503.
- FUJIOKA, S., NISHIMURA, H., NISHIHARA, K., SASAKI, A., SUNAHARA, A., OKUNO, T., UEDA, N., ANDO, T., TAO, Y.Z., SHIMADA, Y., HASHIMOTO, K., YAMAURA, M., SHIGEMORI, K., NAKAI, M., NAGAI, K., NORIMATSU, T., NISHIKAWA, T., MIYANAGA, N., IZAWA, Y. & MIMA, K. (2005a). Opacity effect on extreme ultraviolet radiation from laser-produced tin plasmas. *Phys. Rev. Lett.* **95**, 235004.
- GU, Q.C., NAGAI, K., NAKAI, M. & NORIMATSU, T. (2006). Polymorphic tin dioxide synthesis via sol-gel mineralization of ethyl-cyanoethyl cellulose lyotropic liquid crystals. *Colloid Polym. Sci.* **284**, 429–434.
- GU, Q.C., NAGAI, K., NORIMATSU, T., FUJIOKA, S., NISHIMURA, H., NISHIHARA, K., MIYANAGA, N. & IZAWA, Y. (2005). Preparation of low-density macrocellular tin dioxide foam with variable window size. *Chem. Mater.* **17**, 1115–1122.
- HARILAL, S.S., O’SHAY, B., TILLACK, M.S., TAO, Y., PAGUIO, R., NIKROO, A. & BACK, C.A. (2006). Spectral control of emissions from tin doped targets for extreme ultraviolet lithography. *J. Phys. D: Appl. Phys.* **39**, 484–487.
- HAYDEN, P., CUMMINGS, A., MURPHY, N., O’SULLIVAN, G., SHERIDAN, P., WHITE, J. & DUNNE, P. (2006). 13.5 nm extreme ultraviolet emission from tin based laser produced plasma sources. *J. Appl. Phys.* **99**, 093302.
- HIGASHIGUCHI, T., HAMADA, M. & KUBODERA, S. (2007). Development of a liquid tin microjet target for an efficient laser-produced plasma extreme ultraviolet source. *Rev. Sci. Instr.* **78**, 036106.
- HUND, J.F., PAGUIO, R.R., FREDERICK, C.A., NIKROO, A. & THI, M. (2006). silica, metal oxide, and doped aerogel development for target applications. *Fusion Sci. Technol.* **49**, 669–675.
- KHALENKOV, A.M., BORISENKO, N.G., KONDRASHOV, V.N., MERKULIEV, YU.A., LIMPOUCH, J. & PIMENOV, V.G. (2006). Experience of micro-heterogeneous target fabrication to study energy transport in plasma near critical density. *Laser Part. Beams* **24**, 283–290.

- KOLACEK, K., SCHMIDT, J., PRUKNER, V., FROLOV, O. & STRAUS, J. (2008). Ways to discharge-based soft X-ray lasers with the wavelength $\lambda < 15$ nm. *Laser Part. Beams* **26**, 167–178.
- NAGAI, K. (2008). Nanomaterials to generate extreme ultraviolet (EUV) light. In *Encyclopedia of Nanoscience and Nanotechnology 2nd ed.* (Nalwa, E.H., ed.). Stevenson Ranch, CA: American Scientific Publishers.
- NAGAI, K., AZECHI, H., ITO, F., IWAMOTO, A., IZAWA, Y., JOHZAKI, T., KODAKA, R., MIMA, K., MITO, T., NAKAI, M., NEMOTO, N., NORIMATSU, T., ONO, Y., SHIGEMORI, K., SHIRAGA, H. & TANAKA, K.A. (2005). Foam materials for cryogenic targets of fast ignition realization experiment (FIREX). *Nucl. Fusion* **45**, 1277–1283.
- NAGAI, K., GU, Q.C., GU, Z.Z., OKUNO, T., FUJIOKA, S., NISHIMURA, H., TAO, Y.Z., YASUDA, Y., NAKAI, M., NORIMATSU, T., SHIMADA, Y., YAMAURA, M., YOSHIDA, H., NAKATSUKA, M., MIYANAGA, N., NISHIHARA, K. & IZAWA, Y. (2006b). Angular distribution control of extreme ultraviolet radiation from laser-produced plasma by manipulating the nanostructure of low-density SnO₂ targets. *Appl. Phys. Lett.* **88**, 094102.
- NAGAI, K., NISHIMURA, H., OKUNO, T., HIBINO, T., MATSUI, R., TAO, Y.Z., NAKAI, M., NORIMATSU, T., MIYANAGA, N., NISHIHARA, K. & IZAWA, Y. (2004b). Nanoporous and low-density materials for laser produced extreme uv light source. *Trans. Mater. Res. Soc. Jpn.* **29**, 943–946.
- NAGAI, K., NORIMATSU, T. & IZAWA, Y. (2004a). Control of micro- and nano-structure in ultralow-density hydrocarbon foam. *Fusion Sci. Technol.* **45**, 79–83.
- NAGAI, K., WADA, D., NAKAI, M. & NORIMATSU, T. (2006a). Electrochemical fabrication of low density metal foam with mono-dispersed-sized micro- and submicro-meter pore. *Fusion Sci. Technol.* **49**, 686–696.
- NAGANO, A., INOUE, T., NICA, P.-E., AMANO, S., MIYAOTO, S. & MOCHIZUKI, T. (2007). Extreme ultraviolet source using a forced recombination process in lithium plasma generated by a pulsed laser. *Appl. Phys. Lett.* **90**, 151502.
- NISHIHARA, K., SASAKI, A., SUNAHARA, A. & NISHIKAWA, T. (2006). *Conversion Efficiency of LPP sources*. Bellingham, WA: SPIE Press.
- NISHIHARA, K., SUNAHARA, A. & KANG, Y.G. (2007). *Theoretical Guideline of LPP-EUV Sources for HVM*. Osaka, Japan: ILE Osaka University.
- OKUNO, T., FUJIOKA, S., NISHIMURA, H., TAO, Y., NAGAI, K., GU, Q., UEDA, N., ANDO, T., NISHIHARA, K., NORIMATSU, T., MIYANAGA, N., IZAWA, Y., MIMA, K., SUNAHARA, A., FURUKAWA, H. & SASAKI, A. (2006). Low-density tin targets for efficient extreme ultraviolet light emission from laser-produced plasmas. *Appl. Phys. Lett.* **88**, 161501.
- ORLOV, N.Yu., GUS'KOV, S.Yu., PIKUZ, S.A., ROZANOV, V.B., SHELKOVENKO, T.A., ZMITRENKO, N.V. & HAMMER, D.A. (2007). Theoretical and experimental studies of the radiative properties of hot dense matter for optimizing soft X-ray sources. *Laser Part. Beams* **25**, 415–423.
- PAN, C., GU, Z.Z., NAGAI, K., NORIMATSU, T., BIROU, T., HASHIMOTO, K. & SHIMADA, Y. (2006). SnO₂ target with controllable micro-structure and thickness for generating extreme ultraviolet light. *J. Appl. Phys.* **100**, 016104.
- SHIMADA, Y., NISHIMURA, H., NAKAI, M., HASHIMOTO, K., YAMAURA, M., TAO, Y., SHIGEMORI, K., OKUNO, T., NISHIHARA, K., KAWAMURA, T., SUNAHARA, A., NISHIKAWA, T., SASAKI, A., NAGAI, K., NORIMATSU, T., FUJIOKA, S., UCHIDA, S., MIYANAGA, N., IZAWA, Y. & YAMANAKA, C. (2005). Characterization of extreme ultraviolet emission from laser-produced spherical tin plasma generated with multiple laser beams. *Appl. Phys. Lett.* **86**, 051501.
- SIZYUK, V., HASSANEIN, A. & SIZYUK, T. (2007). Hollow laser self-confined plasma for extreme ultraviolet lithography and other applications. *Laser Part. Beams* **25**, 143–154.
- TAO, Y., FARSHAD, S., NISHIMURA, H., MATSUI, R., HIBINO, T., OKUNO, T., FUJIOKA, S., NAGAI, K., NORIMATSU, T., NISHIHARA, K., MIYANAGA, N., IZAWA, Y., SUNAHARA, A. & KAWAMURA, T. (2004). Monochromatic imaging and angular distribution measurements of extreme ultraviolet light from laser-produced Sn and SnO₂ plasmas. *Appl. Phys. Lett.* **85**, 1919–1921.
- UCHIDA, S., SHIMADA, Y., YAMAURA, M., TAKEMOTO, S., FUJIOKA, S., NISHIMURA, H., NAGAI, K. & NISHIHARA, K. (2005). *Foil Target Acceleration Providing Mass Limited Target for EUV Laser Plasma Source*. Osaka, Japan: ILE Osaka University.
- XU, Y., JIANG, S., LAI, D., PEI, W., EI DING, Y., CHANG, T., LAN, K., LI, S. & FENG, T. (2006). Two-photon group radiation transfer study in low-density foam cylinder. *Laser Part. Beams* **24**, 495–501.
- YANG, H., NAGAI, K., NAKAI, M. & NORIMATSU, T. (2008). Thin shell aerogel fabrication for FIREX-I targets using high viscosity (phloroglucinol carboxylic acid)/formaldehyde solution. *Laser Part. Beams* **26**, doi:10.1017/S0263034608000451
- YASUDA, Y., GU, Q.C., NAGAI, K., NAKAI, M., NORIMATSU, T., FUJIOKA, S., NISHIMURA, H. & NAKATSUKA, M. (2006). Tin-polymer composite target on a rotating drum as high-repeating laser irradiation for extreme ultraviolet generation. *Fusion Sci. Technol.* **49**, 691–694.
- YASUDA, Y., NAGAI, K., NORIMATSU, T., FUJIOKA, S., NISHIMURA, H., NISHIHARA, K., IZAWA, Y. & MIMA, K. (2007). Development of “punching-out target” to generate extreme ultraviolet (EUV) light. *Fusion Sci. Technol.* **51**, 769–771.